MAGNETIC STUDIES ON SINGLE CRYSTALS OF TUNGSTENITE (WS_2)

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ABSTRACT. Tungstenite (WS_2) crystal possesses a structure similar to that of molybdenite (MoS_2). Recent magnetic measurements on single crystals of molybdenite by Dutta revealed some very interesting facts regarding its electronic energy structure. Magnetic measurements on single crystals of tungstenite have therefore been undertaken in this laboratory with a similar objective in view. But unlike molybdenite it was found to be paramagnetic. The paramagnetic susceptibility along the hexagonal axis, $\chi_{\parallel}$, is about 4917×10^{-6} c.g.s. e.m units per gm. mol. at 30°C while $\chi_{\perp}$, that at right angles to the axis is about 6314×10^{-6} c.g.s. e.m. units per gm. mol at the same temperature, which corresponds to an anisotropy of about 24 per cent. These measurements have been extended to various temperatures ranging from 700°K down to about 80°K. The effective magnetic moment along both the directions have been found to have maxima values near about the room temperature and have been found to decrease continuously with either increase or decrease of temperature within the present range. W^{++} ion is in a ground state $5d^2\ ^3F_2$ and the available X-ray data indicate that the crystalline electric field acting on the ion is presumably of a trigonal symmetry. The Stark pattern of the ground state under such a field is shown to be one degenerate doublet lying lowest and one singlet separated from it by several hundred cm^{-1}. On this basis an explanation of the anisotropy and the variation of magnetic moments with temperature has been attempted.

INTRODUCTION

In recent years the study of the properties of semi-conductors have engaged the attention of the theoretical as well as of the experimental physicists. All theoretical investigations on this subject are based on the ideas sponsored by Wilson (1931, 1932, 1939), while a fairly large amount of experimental work on it has been done mainly by the Russian (Gudden, 1934) and the German (Gudden *l. c.*) schools of physicists. But the experimental data are so varied and most often so conflicting and unsystematic that these are not always amenable to any theoretical treatment. Moreover, a study of the behaviour of this class of solids in the state of single crystals, which is expected to furnish the most interesting and essential informations regarding their structure and the structure sensitive physical properties, has been much neglected. It was to elucidate this aspect of the problem that Ganguly and Krishnan (1936, 1941) initiated the studies on single crystals of graphite Instead of, however, investigating directly the electrical conductivity of the substance in the manner of the previous workers in this line, they started with the magnetic properties and arrived at some highly

interesting conclusions. They were able to show from their investigations that the abnormal diamagnetism of graphite is entirely a "free" electronic phenomenon. For a detailed account of the nature of this free electron diamagnetism in graphite, it would be best to refer to their original papers. Continuing in the same line of investigations, Dutta (1944, 1945) showed that the highly unidirectional and large diamagnetism in single crystals of molybdenite (MoS_2), which is known to be a semi-conductor and which possesses a hexagonal structure, has the same origin as that in graphite and the results have been reported in some recent papers.

Tungstenite (WS_2) which possesses a structure similar to that of molybdenite would naturally be expected to be a semi-conductor also. But no data electrical or magnetic are available for this substance so as to be able to verify such an expectation. Consequently it was thought desirable to start an investigation on single crystals of tungstenite. A complication, however, arises due to the fact that unlike the crystals of graphite and molybdenite, tungstenite is found to be strongly paramagnetic. The present paper gives an account of the measurements of the magnetic properties of single crystals of tungstenite at temperatures ranging from 700°K down to about 80°K.

EXPERIMENTAL

Since tungstenite (WS_2) is a hexagonal crystal having a layer lattice, a determination in two directions of the magnetic susceptibility namely, $\chi_\parallel$, in a direction parallel to the hexagonal axis and $\chi_\perp$, that at right angles to the axis are enough. To obtain these values the procedure of Krishnan and his collaborator (1935) is adopted. It essentially consists of :

(*i*) The determination of the principal anisotropy, *i. e.*, the difference $\chi_\parallel - \chi_\perp$ between the principal susceptibilities.

(*ii*) The determination of the absolute value of one of these magnetic susceptibilities.

A short account of the methods of these measurements at room temperatures as well as of the adaptations necessary for extending the measurements to various other temperatures are given below.

MEASUREMENT OF ANISOTROPY

(*a*) *Room temperatures.*—In the particular case of tungstenite, the crystal is suspended vertically along its basal plane in a uniform horizontal magnetic field from one end of a fine calibrated quartz fiber, the other end of which is attached to a graduated torsion head. The crystal tends to bring its basal plane to parallelism with the field, showing that the susceptibility of the crystal along directions in the basal plane, *i.e.*, $\chi_\perp$, is greater than that along the symmetry axis, $\chi_\parallel$. The torsion head is suitably rotated so that when the crystal sets in the magnetic field, there is

no torsion on quartz fibre. If the torsion head be now rotated the crystal will also rotate but through a smaller angle, until there will come a stage, corresponding to a rotation of the torsion head through an angle α_c and of the crystal through an angle of $\frac{\pi}{4}+\sigma_c$, when the equilibrium of the crystal in the field will become unstable and the crystal will turn round suddenly towards the next position of stable equilibrium. It can then be shown that the difference in the maximum and minimum susceptibilities in the horizontal plane of suspension is given by

$$\frac{1}{2}\frac{m}{Mc}H^2(\chi_\perp-\chi_\parallel)=\lambda(\text{say})=\frac{\alpha_c-\pi/4-\sigma_c}{\cos 2\sigma_c} \quad \ldots \quad (1)$$

$$\text{where } \sin 2\sigma_c=\frac{1}{2\lambda} \quad \ldots \quad (2)$$

This equation enables us to determine the value of $\chi_\perp-\chi_\parallel$, the value of m and M, the mass and the molecular weight of the crystal respectively, c, the torsional constant of the fibre and H, the magnetic field strength being previously known. In actual practice the value of the field strength and the dimensions of the fibre are so adjusted that α_c is always sufficiently large so that the factor σ_c may be neglected and the anisotropy $\chi_\perp-\chi_\parallel$ can be expressed by the simpler relation

$$\frac{1}{2}\frac{m}{Mc}H^2(\chi_\perp-\chi_\parallel)=(\alpha_c-\pi/4) \quad (3)$$

(*b*) *Low temperatures.*—For measurements at low temperatures, the crystal is suspended with its basal plane vertical from one end of a long glass rod the other end of which is attached to one end of a fine, calibrated quartz fibre, the other end being attached to a graduated torsion head and the crystal with the major portion of the glass rod is kept hanging inside a gas-flow cryostat designed by Bose (1947) for magnetic measurements with which temperatures down to about 80°K can be attained. The measurement of anisotropy at different low temperatures is then made in the usual manner (Bose, *loc. cit*). By this process measurements can be made at temperatures down to about 80°K.

(*c*) *High temperatures.*—The measurements of anisotropy at higher temperatures are performed in a manner similar to that utilised by Dutta (1945). The suspension of the crystal in this case consists of two parts, the upper one is a fine quartz fibre which has been kept at the room temperature by means of water circulation ; the lower one is a thin pyrex glass rod to the lower end of which the crystal is attached with its basal plane vertical by means of a dental cement which has been previously tested and

found to be very feebly diamagnetic and isotropic. The measurement of anisotropy is then made in the same manner as of Dutta (1945).

MEASUREMENT OF $\perp$. THE MAGNETIC SUSCEPTIBILITY PERPENDICULAR TO THE SYMMETRY AXIS

At room temperatures.—The absolute magnetic susceptibility of tungstenite crystals along directions perpendicular to that of the symmetry axis, $\chi_\perp$, is measured by the method of Dutta (1944) as well as by that of Bose (1947). The method of Dutta (*loc. cit.*) is essentially the method of balancing the horizontal force exerted on the crystal when it is placed in a non-homogeneous magnetic field (the horizontal gradient being only effective) by applying torsion to a horizontally stretched fibre (usually of silver) from the centre of which the crystal is rigidly suspended with its basal plane vertical and kept in the setting position by means of a fine glass rod. The torsional balancing is done by keeping the crystal immersed successively in two liquid media of known volume susceptibilities K_1 and K_2 so that the volume susceptibility of the crystal is given by

$$\frac{K_c - K_1}{K_c - K_2} = \frac{\theta_1}{\theta_2} \qquad \ldots \quad (4)$$

where K_c is the volume susceptibility of the crystal and θ_1 and θ_2 respectively are the angles of torsion needed to balance the magnetic force on the crystal when immersed in the two liquids. The method of Bose (1947) is the method of balancing the vertical force exerted on a crystal suspended in the usual manner from one arm of a torsional micro-balance specially designed by him for magnetic measurements. It is so arranged in his method that the vertical component of the magnetic force is only effective. The torsional balancing is done in this case also in two different liquid media of known volume susceptibilities. The calculation of the volume susceptibility is the same as that in the method of Dutta.

A determination of the density of the crystal will enable us to calculate the value of $\chi_\perp$.

At low temperatures.—The procedure for measuring the absolute susceptibility $\chi_\perp$ of the crystal is the same as that adopted by Bose (1947) for the study of paramagnetic crystals of the iron group of elements at low temperatures.

At higher temperatures.—The measurement of $\chi_\perp$ at higher temperatures was done as in the case of low temperatures by the quartz microbalance the low temperature cryostat being replaced by the heater and using dental cement instead of shellac as the attaching material.

TABLE I

Diamagnetic Correction :

$W^{+4} = -35.19 \times 10^{-6}$
$S^{-2} = -31 \times 10^{-6}$
} 66.19×10^{-6} per gm mol.

At 30°C

Crystal	Anisotropy $(\chi_\perp - \chi_\parallel) \times 10^6$ per gram mol.	Volume susceptibility $K \times 10^6$ per c c	Density	Corresponding gram molecular susceptibility at right angles to the symmetry axis, $\chi_\perp \times 10^6$	Mean anisotropy $(\chi_\perp - \chi_\parallel) \times 10^6$ per gram mol	Mean $\chi_\perp \times 10^6$ (after diamagnetic correction)	Mean gram molecular susceptibility along the symmetry axis, $\chi_\parallel \times 10^6$	Percentage of anisotropy
1	1381	195.1	7.63	6342				
2	1387	182 2	7.00	6457				
3	1501	182.36	7.52	6018	1397.40	6314.19	4916.79	23.89 %
4	1255	205.1	8.2	6203				
5	1463	193.93	7.73	6220				

TABLE II

Temperature °K	$(\chi_\perp - \chi_\parallel) \times 10^6$	$\chi_\perp \times 10^6$	$\chi_\parallel \times 10^6$	$\mu_\perp^2$	$\mu_\parallel^2$	$\bar{\mu}^2$
84	10630	19500	8870	13.33	6.01	10.89
88	10220	19050	8830	13.45	6.27	11.06
100	9080	17300	8220	13.95	6.63	11.51
120	7350	14900	7550	14.41	7.31	12.04
140	5750	12850	7100	14.51	8.02	12.35
160	4500	11250	6750	14.52	8.71	12.58
180	3670	10100	6430	14.66	9.33	12.88
200	3025	9175	6150	14.80	9.92	13.17
250	2000	7450	5450	15.03	10.99	13.68
300	1410	6230	4820	15.07	11.66	13.93
350	1100	5270	4170	14.87	11.77	13 84
400	875	4450	3575	14.35	11.53	13.41
450	720	3800	3080	13.79	11.19	12.92
500	600	3230	2630	13.03	10.61	12.22
550	510	2740	2230	12.15	9.89	11.39
600	410	2300	1890	11.13	9.14	10.47
630	350	2075	1725	10.54	8.77	9.95
650	340	1940	1600	10.12	8.38	9.54
660	310	1860	1550	9.90	8.25	9.35
670	300	1800	1500	9.73	8.11	9.19
680	300	1750	1450	9.59	7.95	9.04

RESULTS

Since the naturally occuring crystal of tungstenite contain varying amounts of impurities depending on the source from which it is obtained, the measurements had to be repeated with a number of specially chosen single crystals so that errors possibly arising out of the presence of impurities was a minimum and consistent. The room temperature measurements on five different single crystals of tungstenite are shown in Table I The values of the susceptibilities are expressed in electromagnetic C. G. S. units. In Table II are given the measurements at temperatures from about 700°K down to about 80°K. The values of $\mu_{\parallel}$ and $\mu_{\perp}$ effective magnetic moments expressed in Bohr magnetons for fields along and at right angles to the axis of symmetry, respectively are calculated according to the relation

$$\chi_i = \frac{N\mu_i^2 \beta^2}{3kT} \qquad i = \parallel \text{ or } \perp \qquad \ldots \quad (5)$$

where N is the Avogadro number, β, the Bohr Magneton number and k is the Boltzman constant. The variation of $\mu_{\parallel}$, $\mu_{\perp}$ and $\mu = \sqrt{\frac{2\mu_{\perp}^2 + \mu_{\parallel}^2}{3}}$ with temperature are also given in Table II. The variation of susceptibilities and effective magnetic moments with temperature are represented graphically in figures 1 and 2 respectively.

CRYSTAL STRUCTURE OF TUNGSTENITE (WS_2) AND THE CHOICE OF CRYSTALLINE FIELD

Like molybdenite, tungstenite is a hexagonal crystal having a layer lattice. The cleavage between the different layers are fairly easy, but not as much as in the case of molybdenite. The structure of tungstenite was determined by van Arkel (1926). The unit cell contains two molecules of tungstenite (WS_2), *i.e.* two atoms of W and four atoms of S. The unit cell has the following dimensions

$$a = 3.18\text{Å}, \quad c = 12.5\text{Å}$$

$$\text{and} \quad \frac{c}{a} = 3.93$$

and the various interatomic distances are

$$W - W = 3.18\ \text{Å}\ ; \quad S - S = 3.18\ \text{Å}\ ; \quad W - S = 2.48\ \text{Å}$$

It is evident that the W-atoms in the crystal are arranged in layers parallel to the basal plane and each such layer is sandwiched between two similar and parallel layers of sulphur atoms. The three layers form a *composite layer*, by the repetition of which the whole structure is built up. The sulphur atoms in the two alternate layers lie directly above one another

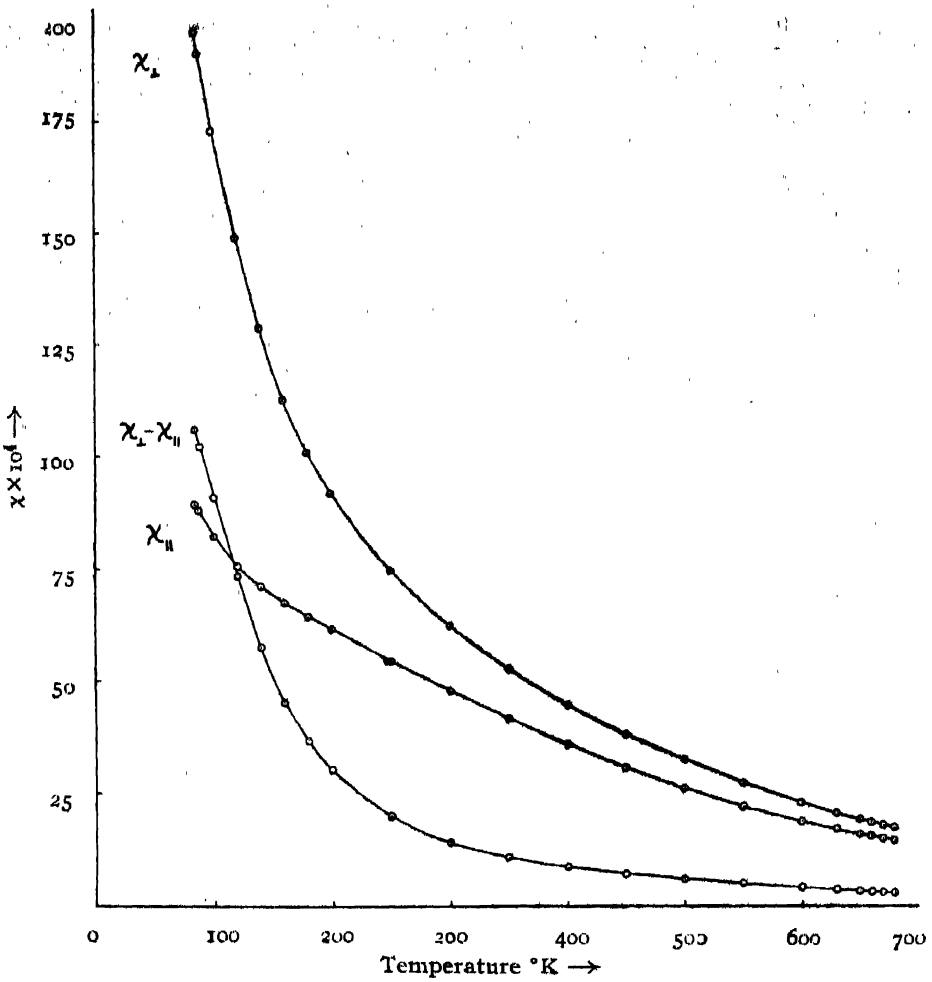

FIG. 1

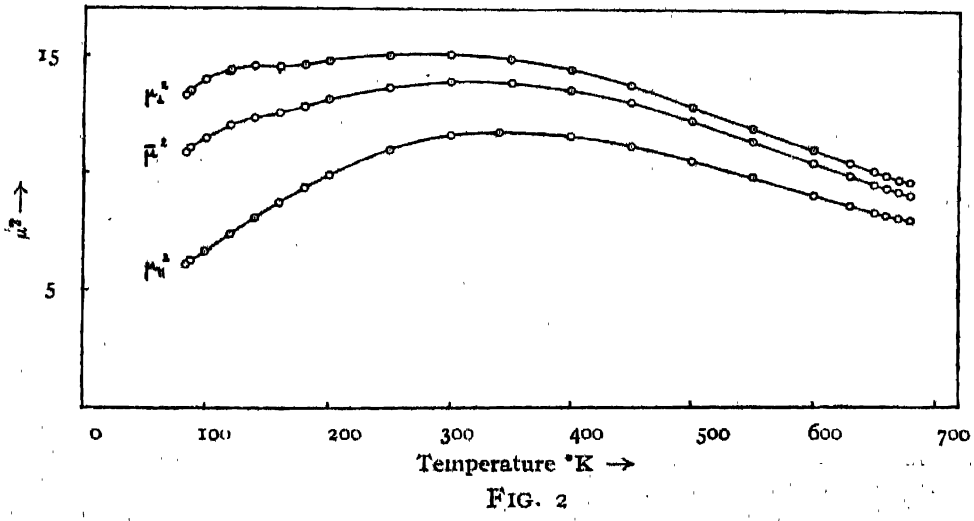

FIG. 2

and each is directly above or below the centre of the triangle formed by the W-atoms in the intermediate layers, and similarly for the W-atoms. The

W-atoms in one composite layer are again directly above or below the sulphur atoms in the next composite layer. Each atom of tungsten is surrounded by six equidistant sulphur atoms which lie at the corners of a right equilateral triangular prism. On the other hand each sulphur atom is equidistant from three tungsten atoms at the corners of an equilateral triangle.

The distance between similar atoms in the same layer W-W or S-S are seen to be much larger than that between dissimilar atoms, W-S. The distance between two adjacent composite layers is also large namely 3.13 Å. This explains the good basal cleavage of the crystal.

Thus in tungstenite (WS_2) crystal the group of six sulphur atoms surrounding each tungsten ion evidently has a trigonal symmetry and hence the crystalline electric field surrounding the central positive ion may be taken to be predominantly cubic one on which a small trigonal component has been super-imposed. Further the two sets of field axes for the two positive ions in the unit cell will be evidently parallel to each other leading to great simplification of the correlation between ionic and crystalline magnetic behaviours.

SPECTROSCOPIC STATE OF THE ION AND CONSIDERATIONS ARISING THEREFROM

Tungsten belongs to the platinum group of metals in which the $5d$ shell, which was left with only one electron until the element lutecium is reached, is in the course of being filled up. In tungsten the $5d$ shell contains 4 electrons and the $6s$ shell 2 electrons. In tungsten sulphide (WS_2) the two $6s$ and two $5d$ electrons take part in bond formation so that the tungsten ion is quadruply charged W^{+4}, and is left with 2 electrons in the incomplete $5d$ shell. According to Hund's theory the assignments of the lowest lying spectral states for the different ions in the $3d$ and $5d$ transition groups of elements are as is shown in Table III for comparison, and it will be seen that W^{+4} ion has a ground state $5d^2\ {}^3F_2$, the same as in the case Ti^{++} and V^{+++} belonging to the iron group of elements. Such identity of spectroscopic

TABLE III

Number of d electrons	0	1	2	3	4	5	6	7	8	9	10
Ground state	$^1S_0$	$^2D_{3/2}$	$^3F_2$	$^4F_{3/2}$	$^5D_0$	$^6S_{5/2}$	$^5D_4$	$^4F_{9/2}$	$^3F_1$	$^2D_{5/2}$	$^1S_0$
Ions of iron group	K^+ V^{+5}	Sc^{++} Ti^{+++} V^{+4}	Ti^{+2} V^{+3}	V^{+2} Cr^{+++} Mn^{+4}	Cr^{++} Mn^{+3}	Mn^{++} Fe^{++}	Fe^{++}	Co^{++}	Ni^{++}	Cu^{++}	Ca^+ Cu^+
Ions of platinum group	Ta^{5+} Hf^{+4}	Ta^{+4} Hf^{+3} Lu^{+2}	W^{+4} Ta^{+3}	W^{+3} Re^{+4}	Re^{+3} W^{+2}	Os^{+3} Re^{+2} Ir^{+4}	Os^{+2} Ir^{+3} Pt^{+4}	Ir^{+2} Pt^{+3}	Pt^{+2} Ir^+ Au^{+3}	Pt^+ Au^{+2}	Au^+_2

ground state with iron group, in fact, occurs throughout the platinum group. We can, in consequence, directly take over many of the considerations in regard to iron group, as being applicable to the platinum group also. For example, from the spectroscopic state we can at once calculate the effective magnetic moment for the "free" W^{+4} ion which comes out as 1·63 Bohr magnetons while the "spin only" value is 2·83. On the other hand it is known that in the heavier atoms such as of the rare-earth elements or the platinum group elements the multiplet width is very large (Laporte, O , 1928). So that the coupling between L and S is not easy to break under the action of external electric fields. In the rare-earth ions this is more so because the $4f$ electrons are protected from the effect of external electric fields by outer complete shells of electrons. In consequence, the ions in both these groups should be expected to behave as if they are more or less free. Even though they may not exactly correspond with the Hund's value for the "free ion" calculated on the assumption that the overall multiplet width is infinitely large, the very small action of the crystalline field will not lead to a quenching of the orbital moment as apart from the spin moment ; but will at best lead to a restriction of the orientation of the J moment as a whole (Penney and Schlapp, 1932). Experimental investigations on rare-earth salts agree very well with such contentions (Selwood, 1943; Mookerjee).* But accurate data on platinum and other heavy group salts is very meagre. Some of the data available (Bose, D.M., 1927 ; Van Vleck, 1932 ; and Selwood, 1943) on a few compounds of Mo^{+++} and Ru^{+4} of the molybdenum group, of W^{+3} and W^{+4} of the platinum group and of U^{+4} of the uranium group seem indeed to show the validity of such a conclusion in these salts also. But we should be very cautious in accepting such an interpretation of the experimental data, in view of a number of complicating factors which will be introduced in the next section.

NATURE OF CHEMICAL BINDING AND THE CRYSTALLINE ELECTRIC FIELD

We should remember that in the platinum group the $5d$ electrons are not at all screened from the action of the external fields. Further, though the spin-orbit coupling is generally high in the platinum group of elements it is not relatively so high in the earlier elements in the group as in the latter. Lastly, it is well known that the elements of the platinum group have a strong tendency for the formation of covalent bonds in which the bond energy is very much higher than in ordinary ionic bonds. In tungsten sulphide, for example, the two sulphur atoms are known to be bound to the tungsten by a pair of double covalent bonds, the W-S distance being 2.48 Å. In such cases of complex formations the crystalline field will be exceedingly high and may break down totally the Russel-Saunders coupling not only of L's and S's but even between individual l's and s's. The electrons in the

* A. Mookerjee, unpublished work, part of a thesis for D.Sc. degree, kindly communicated to the senior author.

incomplete shell will then have to be assigned to different $5d$ orbitals, which are left over after suitable assignment has been made of the electrons taking part in the covalent bonds. In this process those electrons which are not paired in the orbitals will contribute to the spin moment of the ion, orbital moment having been completely quenched except for small "high frequency" contributions. It will be seen that in such cases when spins pair off completely the substance will become diamagnetic altogether. Evidence for such covalent complex formations is obtained in large numbers in not only iron group elements but to an even larger extent in palladium and platinum groups. A study of the magnetic behaviour of these groups of salts shows a very large number of cases in which the effective magnetic moment is abnormally low and quite often zero. This is, in fact, observed even in such ions as Ru^{+3} Os^{+3} Ir^{+4} (Selwood, 1943) which are in the S-state and hence on which the crystalline field should ordinarily have little direct influence. Thus, a low value of effective moment in the first half of the transition group should rather be ascribed to such covalent bond formation rather than to free ion behaviour as might appear at first sight. Intermediate cases must also be sometimes met with, *i.e.*, compounds in which the covalent bond field may not be so high as to split altogether the l's and s's but still high enough leading only to a splitting of L and S, since L-S coupling is strong comparatively to the iron group. Such a case is exactly analogous to the ordinary ionic salts of the iron group. It is *presumably* this state of affairs which we come across in tungsten sulphide. The experimental investigations undertaken by us over a wide range of temperatures indeed points to such a conclusion. From the table of data (Table II) for the effective magnetic moment of the W^{+4} ion we see that the mean magnetic moment of the crystal varies only moderately and at room temperature the value is 3·732 Bohr magnetons, which is widely different from the "free" ion value of 1·63, and even greater than the "spin only" value of 2·83. This evidently signifies that the spin orbit coupling is not so high as to remain unaffected by the crystalline field nor is the latter so high as to produce a complete breakdown of the L-S coupling. On the other hand, moderately large orbital contributions acting in the same direction as the spin contribution comes, giving a value in excess of the "spin only" value. The deviation from Curie law of temperature variation of the effective magnetic moment is also moderately large and complicated as will be seen from the Table II. Finally, the crystal is found to have a large anisotropy of the order of about 24%. These two latter facts also rule out not only a "free ion" hypothesis but also a complete breakdown of Russel-Saunders coupling for W^{+4} ion in tungstenite. The explanation of the afore-mentioned behaviour hence, must be that in spite of the generally wide multiplet separation in the group the covalent co-ordination of the W^{+4} ion with the sulphur atoms are such as to break down partially the L-S coupling of the $5d$ electrons and lead to a crystalline Stark splitting of the same nature as in the case of the ionic salts of the iron group.

THE STARK PATTERN OF THE GROUND STATE OF THE W^{++} ION AND THE EFFECTIVE MAGNETIC MOMENT

From what we have said before regarding the different spectroscopic states of the ions it will be seen that W^{++} ion, in common with Ti^{++} and V^{+++} belonging to the iron group of elements, has a ground state $^3F_2$.

In our earlier discussion about the nature of the crystalline field in WS_2 crystal we noted that the central tungsten ion is at the centre of an equilateral triangular prism the six corners of which are occupied by six sulphur atoms. This as is evident would give us a trigonal electric field with its axis of symmetry coinciding with the hexagonal axis of the crystal. Van Vleck (1939) and Siegert (1936) have shown that in titanium and vanadium alums, in both of which the paramagnetic ions are *trivalent*, the crystal field which has to be chosen from X-ray data on the crystals is of a trigonal character superposed on a predominant cubic field. Under such a trigonal field the Stark splitting of the degenerate cubic components in Ti^{+++} is given as in Fig. 3*a*, *i.e.*, a doublet of which

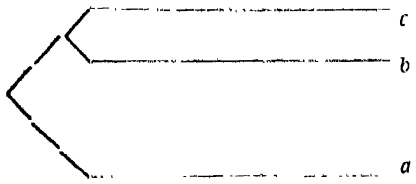

Fig. 3*a*

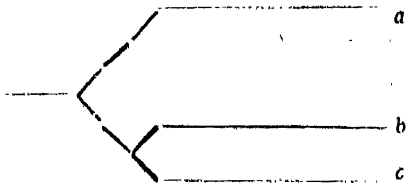

Fig. 3*b*

the lower component is orbitally nondegenerate but the upper level retains its orbital degeneracy in spite of the trigonal field. It is further shown by Van Vleck (1939) that except under certain special circumstances the pattern suffers an inversion as we pass from one electron Ti^{+++} to two electron V^{+++} *i.e.*, the degenerate state comes lowest for V^{+++} (see Fig. 3*b*). It is evident that in the case of W^{++} also, in WS_2 crystal, since it has the same electron configuration as V^{+++} we can take a similar Stark-splitting of the ground state under the existing trigonal field, with an inversion of the pattern as in V^{+++}. The trigonal separation postulated by Van Vleck (1939) is of the order of a few hundred cm^{-1} and we can in our case assume a separation of the same order from our previous arguments. Magnetic moment in this case will not only depend on the degenerate level *bc* but also upon the level *a*, since the separation between $bc \rightarrow a$ is ordinarily comparable to kT. The orbital contribution should therefore, be fairly large as has been actually found by us experimentally. The distribution of population amongst the various split levels will evidently depend upon temperature and in consequence we should expect complicated variation of the magnetic moment with temperature.

Actually, from the Table II, we see that along the hexagonal axis of the crystal the value of the effective magnetic moment at 84°K is 2.45 Bohr magnetons and gradually increases to a maximum of about 3.431 near about

330°K and decreases again and there is a tendency of its attaining an approximately constant value of 2.82 near about the highest observed temperature of about 700°K. A very similar temperature variation is observed also along directions in the hexagonal plane of the crystal, the value rising from 3.651 at 84°K to a maximum of 3.880 at about 300°K decreasing after this and tending to attain nearly a constant value of 3.100 at about 700°K. The temperature variation of the moment will, to a first approximation, be due to two parts, one obeying a Curie law due to the lowest degenerate doublet level in the Stark pattern, the other due to a change in the relative population of the two levels of the trigonal Stark pattern separated by a few hundred cm^{-1} and will thus give an effective moment first increasing with temperature then decreasing and finally having a tendency of becoming constant.* A simple calculation will show that the assumed order of separation of the trigonal components will actually lead to a maximum in the effective magnetic moment curve in the region of room temperature but afterwards when the contribution from the lower level diminishes more rapidly with temperature the value of the effective moment will decrease and then become constant again as the separation becomes small compared to kT at sufficiently high temperatures. It is also obvious that since the orbital contribution comes chiefly from the lower degenerate component, as this level becomes depopulated at high temperatures the constant value which the effective moments tend to attain should be more or less the 'spin only' value 2·83. This is also verified.

LARGE ANISOTROPY OF THE WS_2 CRYSTAL

As the main orbital contribution to the effective magnetic moment in a particular direction in the crystal depends inversely on the frequency corresponding to the separations between the levels $bc \rightarrow a$, the contribution to the effective moment will be confined mainly to one direction namely the hexagonal axis of the crystal which coincides with the trigonal axis of the field. Further, the absolute value of the effective spin moment being small the ratio of the orbital to spin contribution is large. Thus the anisotropy of the crystal will be very high. It will be interesting to note that actually the value of $\mu_\parallel$ is smaller than $\mu_\perp$ which is readily understood when we remember that W^{+4} belongs to the first half of the group in which the orbital contribution acts against the spin. Again it is in this very direction that the temperature variation of the moment is the larger. Lastly the high frequency contributions are not at all negligible as will be evident from the deviation from spin only value even at high temperatures in the direction of $\mu_\perp$, where low frequency orbital contribution is not of much importance.

It may be mentioned finally that since the W^{+4} ion is surrounded by six sulphur ions and W—W distance fairly large namely 3.18 Å, the exchange

* It should be remembered that the contribution to the moments from "high frequency" terms is directly proportional to the temperature and will somewhat modify the above variations according to its magnitude.

interaction between the W^{+4} ions may not be of very great importance at least within the temperature range employed by us. A preliminary investigation on the WS_2 crystal at varying field strength failed to show any field dependence of the effective moment at ordinary temperatures and hence the exchange or magnetic dipole interactions may be for the present purpose excluded.

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